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"A New Method for the Preparation of Fluorodisulfate Salts"

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University of Washington

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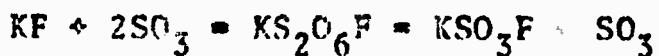
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Contribution from the Department of Chemistry  
University of Washington, Seattle, Washington

"A New Method for the Preparation  
of Fluorodisulfate Salts"

By Darryl D. Des Marteau and George H. Cady

The only reported fluorodisulfate salt is that of potassium. It was prepared by the reaction of potassium fluoride with excess sulfur trioxide.<sup>1</sup>



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1. H. A. Lehmann and L. Kolditz, *Z. Anorg. Allgem. Chem.*, 272, 69 (1953).

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The white crystalline compound was unstable and decomposed completely to potassium fluorosulfate and sulfur trioxide when heated to 100° for 4 hours. Calcium fluorodisulfate has been suggested as an intermediate in the reaction of calcium fluoride with sulfur trioxide.<sup>2</sup>

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2. E. L. Meutterties and D. D. Coffman, *J. Am. Chem. Soc.*, 80, 5914 (1958).

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Potassium, sodium and, probably, ammonium fluorodisulfates have now been produced by reaction of peroxydisulfuryl difluoride with the corresponding peroxydisulfates, the potassium and sodium

$$M_2S_2O_8 + S_2O_6F_2 = 2MS_2O_6F + O_2 = 2MOSO_2F + 2SO_3 \quad (M = K, Na \text{ or } NH_4)$$

salts being obtained in high yield. The ammonium salt was impure and was obtained in approximately 15% yield.

### Experimental

Reagents.— Peroxydisulfuryl difluoride was prepared and purified by the method of Shreeve and Cady.<sup>3</sup> The peroxydisulfate salts

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3. J. M. Shreeve and G. H. Cady, Inorg. Chem., 2, 466 (1963).

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were obtained from commercial sources and were dried by heating in vacuo.

Preparation and Analysis.—The reactions were run in a Pyrex glass bulb fitted with a Fischer-Porter glass valve closed by a Teflon stem.  $S_2O_6F_2$  was condensed onto the dried, powdered peroxydisulfate at  $-183^\circ$  and the mixture was then allowed to warm to room temperature. A slow reaction took place near room temperature liberating oxygen. An approximate 10:1 mole ratio of  $S_2O_6F_2$  to  $M_2S_2O_8$  was used in each case. The reactions were very slow and became slower with time, probably due to surface effects. Oxygen was removed periodically by pumping on the reaction vessel at  $-183^\circ$ . After no further oxygen was observed to form (21 days for 1.7384g  $K_2S_2O_8$ , 4 days for 1.033g  $Na_2S_2O_8$ , 8 days for 1.0356g  $(NH_4)_2S_2O_8$ ), the excess  $S_2O_6F_2$  was removed by pumping at room temperature until the rate of weight loss was only a few mg. per hr. The products could not be pumped to constant weight because the unstable fluorodisulfate salts dissociated slowly into  $SO_3$  and  $MO_2F$  at room temperature. For the above samples of  $K_2S_2O_8$  and  $Na_2S_2O_8$  the weights of product were 2.743g and 1.716g respectively (Theory: 2.807g

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and 1.56g). For the sample of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  the weight of product was 1.169g (1.789g theor) and corresponded to approximately 15%  $(\text{NH}_4)_2\text{S}_2\text{O}_5\text{F}$  mixed with 35%  $\text{NH}_4\text{SO}_3\text{F}$ . The products were then heated to  $135^\circ$  maximum and pumped to constant weight. After this treatment the above samples weighed 1.760, 1.073 and 1.035 g. respectively, corresponding closely to the theoretical weights, 1.770, 1.060 and 1.063 g. respectively for  $\text{KSO}_3\text{F}$ ,  $\text{NaSO}_3\text{F}$  and  $\text{NH}_4\text{SO}_3\text{F}$ .

Other runs were similar to those just described. The  $\text{KOSO}_2\text{F}$ ,  $\text{NaOSO}_2\text{F}$  and  $\text{NH}_4\text{OSO}_2\text{F}$  were then hydrolyzed in 1N. sodium hydroxide for 10 hours at  $100^\circ$  and the resulting solutions were analyzed for sulfur and fluorine. Sulfur was determined gravimetrically as barium sulfate and fluorine volumetrically by the method of Willard and Winter.<sup>4</sup> The sulfur trioxide was identified qualita-

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4. H. H. Willard and O. B. Winter, Ind. Eng. Chem., Anal. Ed.,  
5, 7 (1933).

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tively by its physical properties, by tendency to liberate iodine from aqueous potassium iodide and by giving a positive test for sulfate after hydrolysis. Oxygen was identified by its mass spectrum and volatility at  $-183^\circ$ . The infrared spectrum of the excess peroxydisulfuryl difluoride remaining after reaction corresponded to  $\text{S}_2\text{O}_6\text{F}_2$  containing a trace of  $\text{SiF}_4$ . Analytical data for the runs given above are summarized in table I.

X-ray powder photographs were taken for samples of  $\text{KOSO}_2\text{F}$  and  $\text{KS}_2\text{O}_6\text{F}$  prepared by the method given above and by the method of Lehmann and Kolditz.<sup>1</sup> The two methods gave materials having essentially the same patterns. These are given in the

Table I  
Analytical Data

Cation	Na <sup>+</sup>	K <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>
Moles O <sub>2</sub> <sup>a</sup>	0.98	0.99	1.02
Moles SO <sub>3</sub> <sup>b</sup>	0.99	1.00	1.01
Wt % S <sup>c</sup> found	16.2	13.6	16.0
calc.	15.6	13.8	16.2
Wt % S <sup>c</sup> found	26.2	22.5	27.6
calc.	26.3	23.2	27.3

a per mole of M<sub>2</sub>S<sub>2</sub>O<sub>8</sub> consumed

b per mole MS<sub>2</sub>O<sub>6</sub>F decomposed by heating

c analysis of MOSO<sub>2</sub>F

Ph.D. thesis of the junior author.<sup>5</sup> When the patterns were com-

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S. Darryl D. Des Marteau, Thesis, University of Washington, 1966.

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pared with those reported by Lehmann and Kolditz<sup>1</sup> the extent of agreement was incomplete. Prof. Dr. Kolditz has also compared the data and powder patterns (private correspondence) and agrees with us that the materials obtained by the two methods must be the same even though the reported powder patterns are not exactly the same.

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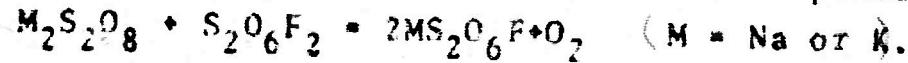
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24. ABSTRACT

Potassium and sodium fluorodisulfates are produced by the reaction of peroxydisulfuryl difluoride with the corresponding peroxydisulfates:

When M is ammonium, some  $NH_4S_2O_6F$  is obtained together with much  $NH_4SO_3F$ , apparently formed by the reaction:

KEY WORDS

LINE A

LINE B

LINE C

HOLE WT HOLE WT HOLE WT

Fluorodisulfate salts